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(54) BINDER RESIN COMPOSITION AND ITS PRODUCTION AND USE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a uniform transparent reaction liquid and a composition having good adherence even to a polyolefin by the graft copolymerization of a carboxylated, chlorinated polyolefin, a monomer containing an ethylenically unsaturated bond in the molecule, and a monomer containing both an ethylenically unsaturated bond and a hydroxyl group in the molecule.

SOLUTION: The carboxylated, chlorinated polyolefin (A) comprises the one grafted with at least one unsaturated carboxylic acid monomer selected from carboxylic acids and/or carboxylic acid anhydrides at a graft ratio of 1-10 wt.% and has a chlorine content of 5-50 wt.%. An example of the monomer (B) containing an ethylenically unsaturated bond in the molecule is (meth)acrylic acid.



The monomer (C) containing both an ethylenically unsaturated bond and a hydroxyl group in the molecule is represented by the formula (wherein R is H or methyl; (m) is 1 to 4; and (n) is 1 to 3), for example, a (meth)acrylic ester modified with dimethyltrimethylene carbonate. The reaction ratio of component A to the total of component B and component C is (90/10) to (10/90). It is desirable that the content of hydroxyl groups in the composition is 0.1-5 wt. %.

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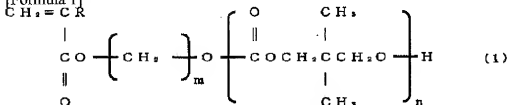
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CLAIMS

[Claim(s)]

[Claim 1] The binder resin constituent with which the rate of a graft of at least one sort of unsaturated-carboxylic-acid monomers chosen from the carboxylic acid and/or the carboxylic anhydride carries out the graft copolymerization of the monomer which contains an ethylene nature unsaturated bond and a hydroxyl group in 1 molecule shown in the monomer and the following general formula (1) which contain an ethylene nature unsaturated bond in 1 molecule to the carboxyl group content chlorinated polyolefins whose chlorine content is 5 - 50 % of the weight, and is obtained at 1 - 10 % of the weight.

[Formula 1]

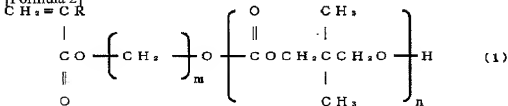


式中のRはHまたはCH₃。mは1～4の整数。nは1～3の整数。

[Claim 2] The binder resin constituent according to claim 1 whose hydroxyl-group content is 0.1 - 5 % of the weight.

[Claim 3] The manufacture approach of a binder resin constituent that the rate of a graft of at least one sort of unsaturated-carboxylic-acid monomers chosen from the carboxylic acid and/or the carboxylic anhydride is characterized by carrying out the graft copolymerization of the monomer containing a hydroxyl group to an ethylene nature unsaturated bond into 1 molecule which chlorine content shows in the monomer and the following general formula (1) which contain an ethylene nature unsaturated bond in 1 molecule at the carboxyl group content chlorinated polyolefins which are 5 - 50 % of the weight at 1 - 10 % of the weight.

[Formula 2]



式中のRはHまたはCH₃。mは1～4の整数。nは1～3の整数。

[Claim 4] The primer which can apply a binder resin constituent according to claim 1 or 2 to the film of the polyolefine system made into an active principle, a sheet, and molding.

[Claim 5] The film of the polyolefine system which makes an active principle a binder resin constituent according to claim 1 or 2, a sheet, the coating that can apply to molding.

[Claim 6] The film of the polyolefine system which makes an active principle a binder resin constituent according to claim 1 or 2, a sheet, ink that can apply to molding.

[Claim 7] The film of the polyolefine system which makes an active principle a binder resin constituent according to claim 1 or 2, a sheet, adhesives that can apply to molding.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the constituent used as the primer which is excellent in the adhesion which was excellent to these sheets and films, and molding in more detail, or other physical properties, a coating, printing ink, or binder resin for adhesives about the binder resin constituent used for the purpose of protection or beautiful decoration of polyolefine system resin, for example, polypropylene, polyethylene, an ethylene propylene copolymerization object, an ethylene propylene diene copolymerization object, etc.

[0002]

[Description of the Prior Art] The degree of freedom of plastics of a design is large by the sex from Takao, and since there are many advantages, such as a light weight, rust proofing, and shock resistance, it is widely used as ingredients, such as autoparts, an electrical part, and construction materials, in recent years. Since polyolefine system resin has the property the price excelled [property] in many, such as a moldability, chemical resistance, thermal resistance, a water resisting property, and a good electrical property, at a low price, it is broadly used as an industrial ingredient and is especially one of the ingredients with which the elongation of the need will be expected most in the future. However, unlike the synthetic resin which has a polarity, such as polyurethane system resin, polyamide system resin, acrylic resin, and polyester system resin, polyolefine system resin has the fault said that paint and adhesion are difficult for a non-polarity and crystallinity.

[0003] Then, conventionally, although adhesion is improved for the front face of a polyolefine system resin moldings plasma treatment and by carrying out gas flame processing and being activated, this approach has a fault, such as producing variation in a surface treatment effect, under the pigment in the complexity of being accompanied by the installation cost complicated [a process] and great or the time loss, and the form of a moldings, and resin, or the effect of an additive.

[0004] As an approach of painting without such pretreatment, a primer constituent which is looked at by polypropylene bumper paint of an automobile is proposed variously, and many chlorinated polyolefins which especially have strong adhesion force to polyolefine system resin are used. However, since the resistance over ultraviolet rays or heat was inferior in chlorinated polyolefins, it could not say that it had sufficient paint film engine performance, but these amelioration was desired strongly. As a means to improve these, the attempt which mixes and uses acrylic resin and the alkyd resin which have good coating physical properties is made. However, since acrylic resin and an alkyd resin originally have chlorinated polyolefins and bad compatibility, the gloss of a paint film falls and problems, such as spoiling an appearance remarkably, are produced.

[0005] In order to improve these faults to JP,58-71966,A To the constituent for covering obtained by copolymerizing, and JP,59-27968,A, an acrylic monomer and chlorinated polyolefins The chlorinated-polyolefins denaturation hydroxyl-group content acrylic copolymer to which copolymerization of the acrylic monomer which has a hydroxyl group, and the chlorinated polyolefins was carried out. To the coating constituent which changes as an indispensable component, and JP,62-95372,A, an isocyanate

compound The adhesives resin constituent which changes considering chlorinated polyolefins, the acrylic monomer which has a hydroxyl group under existence of liquid rubber and the copolymerized hydroxyl-group content acrylic denaturation chlorinated polyolefins, and an isocyanate compound as a principal component, To JP,5-9428,A and JP,5-194910,A Chlorinated polyolefins are copolymerized with a long-chain hydroxyl-group content vinyl monomer, unsaturated carboxylic acid, an unsaturated polyester resin, etc., and the constituent of ** [come / to contain an isocyanate compound, and an ultraviolet ray absorbent and an antioxidant] is proposed. However, since reactivity of chlorinated polyolefins with the copolymeric monomer and resin which were essentially described above is bad, even if it copolymerizes with these, nebula and bilayer separation are produced, a uniform and transparent solution is not obtained, and binder resin, such as a good coating, a primer, and adhesives, cannot become.

[0006] this invention person etc. has already proposed the approach of obtaining uniform and transparent binder resin, by Japanese Patent Application No. No. 506386 [eight to]. That is, it is the approach of making the mixture of the carboxyl group content chlorinated polyolefins chlorinated after carrying out the graft polymerization of alpha and beta-unsaturated carboxylic acid and/or its anhydride to polyolefine, and the chlorinated polyolefins oxidized during the chlorination reaction of polyolefine using at least one sort chosen from air, oxygen, and ozone, or two sorts or more carrying out the graft of the monomer containing an ethylene nature unsaturated bond and a hydroxyl group into the monomer which contains an ethylene nature unsaturated bond in 1 molecule, and/or 1 molecule. However, this approach was also what has the fault that chlorinated polyolefins become unstable in order to oxidize with oxygen etc. during a chlorination reaction, and the constituent compounded as a result becomes unstable, although excelled as an approach of obtaining uniform and transparent binder resin.

[0007]

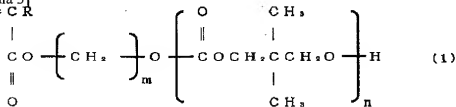
[Problem(s) to be Solved by the Invention] This invention improves the instability which is the fault of the constituent proposed by Japanese Patent Application No. No. 506386 [eight to], solves the above problems, and aims at offering binder resin, such as the coating and primer which are farther [than the conventional chlorinated-polyolefins denaturation object] excellent, printing ink, and adhesives.

[0008]

[Means for Solving the Problem] The rate of a graft of at least one sort of unsaturated-carboxylic-acid monomers chosen from the carboxylic acid and/or the carboxylic anhydride this invention person etc. at 1 - 10 % of the weight to namely, the carboxyl group content chlorinated polyolefins whose chlorine content is 5 - 50 % of the weight It came to accomplish a header and this invention for the binder resin constituent obtained by carrying out the graft copolymerization of the monomer containing a hydroxyl group to an ethylene nature unsaturated bond in 1 molecule shown in the monomer and the following general formula (1) which contain an ethylene nature unsaturated bond in 1 molecule attaining the above-mentioned purpose.

[0009]

[Formula 3]
 $\text{C H}_2 = \text{C R}$



式中のRはHまたはCH₃。mは1～4の整数。nは1～3の整数。

[0010]

[Embodiment of the Invention] The carboxyl group content chlorinated polyolefins used for this invention The melting resin of the polyolefine which carried out thermofusion of the polyolefine, and

carried out degradation by the pyrolysis when required After carrying out the graft copolymerization of the unsaturated-carboxylic-acid monomer to the bottom of existence of a radical generating agent with a batch process or continuous system, Distribute or dissolve in water, a carbon tetrachloride, or the solvent like chloroform, and it puts under existence of a radical generating agent or the exposure of ultraviolet rays. After blowing chlorine gas and carrying out a chlorination reaction in a 50-120-degree C temperature requirement under pressurization or ordinary pressure, a solvent is distilled off, and while adding a stabilizer, it can obtain as a solution article permuted by organic solvents, such as toluene and a xylene. Moreover, after carrying out vacuum concentration of the chlorination solvent after chlorinating, and adding a stabilizer, it can also obtain as a solid from which the solvent was completely removed with the extruder with a vent which installed the vent-port for carrying out reduced pressure distilling off of the solvent.

[0011] As a radical generating agent, there are peroxide like for example, G tert-*****-*****, tert-butyl hydroperoxide, JIKUMIRUPA-oxide, *****-*****, tert-butylperoxide benzoate, methylethyl KETOMPA-oxide, and G tert-BUCHIRUJIPA-phthalate and azonitrile like azobisisobutyronitril.

[0012] Moreover, as the unsaturated-carboxylic-acid monomer used for a graft copolymerization reaction, and its anhydride, there are an acrylic acid, a methacrylic acid, a maleic acid, a maleic anhydride, a citraconic acid, an anhydrous citraconic acid, a fumaric acid, mesaconic acid, an itaconic acid, itaconic acid anhydride, aconitic acid, anhydrous aconitic acid, etc., for example.

[0013] The stabilizer used for the polyvinyl chloride which is chlorine-based resin as a stabilizer of these chlorinated polyolefins can apply as it is. For example, they are organometallic compounds, such as inorganic-acid salts, such as metallic soap, such as calcium stearate and lead stearate, a lead oxide, and tribasic lead sulphate, a dibutyl tin JIRAU rate, and dibutyltin maleate, a hydrotalcite compound, and epoxy compounds.

[0014] However, most generally the epoxy compound is used in this. For example, it is epoxidized soybean oil and the epoxidation linseed oil which carried out epoxidation of the vegetable oil which has a natural partial saturation radical by peroxy acids, such as a peracetic acid. Moreover, they are for example, the epoxidation fatty acid ester which carried out epoxidation of the unsaturated fatty acid ester, such as oleic acid, talloil fatty acid, and a soybean-oil fatty acid, the epoxidation alicyclic compounds which are represented by epoxidation tetrahydro phthalate, the bisphenol A glycidyl ether which condensed bisphenol A, polyhydric alcohol, and epichlorohydrin, ethylene glycol glycidyl ether, propylene glycol glycidyl ether, glycerol polyglycidyl ether, sorbitol polyglycidyl ether, etc. Moreover, butyl glycidyl ether, 2 - Ethylhexyl glycidyl ether, the decyl glycidyl ether, stearyl glycidyl ether, allyl glycidyl ether, phenyl glycidyl ether, sec-buthylphenyl glycidyl ether, tert - They are the mono-epoxy compounds represented by buthylphenyl glycidyl ether, phenol polyethylene oxide glycidyl ether, etc.

[0015] After using the carboxyl group content chlorinated polyolefins used for this invention as the solution article of the chlorinated polyolefins which chlorinated polyolefine by the above-mentioned approach, carrying out the graft copolymerization of an unsaturated-carboxylic-acid monomer and its anhydride to the bottom of existence of a radical generating agent can also obtain them. The above-mentioned thing can use the radical generating agent used for a graft copolymerization reaction, an unsaturated-carboxylic-acid monomer, and its anhydride as it is.

[0016] The unsaturated-carboxylic-acid monomer in carboxyl group content chlorinated polyolefins and the rate of a graft of the anhydride have 1 - 10 desirable % of the weight. The rate of a graft becomes inadequate [graft reactivity with the monomer which has an ethylene nature unsaturated bond as it is less than 1 % of the weight], reaction mixture becomes cloudy or bilayer separation is carried out. If the rate of a graft exceeds 10 % of the weight, it will gel to graft reaction time with the monomer which has an ethylene nature unsaturated bond, or adhesion with polyolefine will worsen.

[0017] Moreover, the chlorine content of carboxyl group content chlorinated polyolefins has 5 - 50 desirable % of the weight. If chlorine content is too low, a solution condition will worsen, and if chlorine content is too high, adhesion with polyolefine will worsen.

[0018] As a raw material of the carboxyl group content chlorinated polyolefins of this invention,

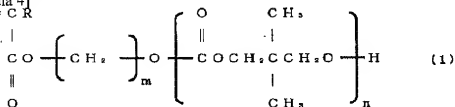
although crystalline polypropylene, i.e., isotactic polypropylene, and syndiotactic polypropylene can be used, generally the former is used. Weight average molecular weight can use the thing of 10,000-300,000.

[0019] Moreover, a propylene-alpha olefin copolymerization object can be used as a raw material. That is, an alpha olefin is copolymerized in this as a subject, and random copolymerization either a block copolymerization object or an object can use a propylene. As an alpha olefin component, ethylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 4-methyl-1-pentene, etc. can be illustrated, for example. If 50-98-mol% of the content of a propylene component is the optimal and is less than [50 mol %], the adhesion over polypropylene will fall. Moreover, if 98-mol % is exceeded, the flexibility of a paint film will worsen.

[0020] As a monomer which contains an ethylene nature unsaturated bond in 1 molecule used for this invention For example An acrylic acid, methyl (Meta) Acrylate, ethyl (Meta) Acrylate, n-butyl (Meta) There are acrylate, 2-ethylhexyl (meta) acrylate, cyclohexyl (meta) acrylate, lauryl (meta) acrylate, glycidyl (meta) acrylate, styrene, vinyl acetate, acrylonitrile (meta), etc. (Meta) Compounds, such as a macro monomer which has the acryloyl radical in which a polymerization is possible (meta), can also be used for the end of polystyrene or Pori (meta) acrylate.

[0021] The monomer which contains an ethylene nature unsaturated bond and a hydroxyl group in 1 molecule shown in the following general formula (1) used for this invention is a compound which has the structure shown in a bottom type and is named generically by dimethyl trimethylene carbonate denaturation (meta) acrylic ester.

[Formula 4]
 $\text{C H}_2 = \text{C R}$



式中のRはHまたは CH_3 。mは1～4の整数。nは1～3の整数。

That is, the compound represented by acrylic ester (meta) is four kinds, methyl (meta) acrylate, ethyl (meta) acrylate, propyl (meta) acrylate, and butyl (meta) acrylate. Since uniform and transparent reaction mixture will not be obtained if m exceeds 4, it is not desirable. Moreover, since uniform and transparent reaction mixture will not be obtained if 3 is exceeded for the integer of 1-3, n of a JIMECHIRUTORI carbonate part is not desirable.

[0022] 0.1 ~ 5wt% of the amount of the hydroxyl group introduced by this monomer is desirable in the binder resin obtained by carrying out graft copolymerization. 0. If it is less than [1wt%], even if it will carry out graft copolymerization, reaction mixture detaches by nebula or the bilayer and a uniform and transparent solution is not obtained. If 5wt(s)% is exceeded, it may gel during a graft copolymerization reaction, and the adhesion over polyolefine also worsens.

[0023] After diluting carboxyl group content chlorinated polyolefins with a solvent suitably, warming them subsequently and adding a polymerization initiator, it makes to react adding a monomer gradually into a basic process, but the reaction approach which carries out the graft copolymerization of the monomer containing an ethylene nature unsaturated bond and a hydroxyl group into the monomer which contains an ethylene nature unsaturated bond in carboxyl group content chlorinated polyolefins and 1 molecule, and 1 molecule mixes a monomer beforehand, after it adds a polymerization initiator, may be warmed and may react.

[0024] The solvent used for a reaction does not interfere, even if aromatic solvents, such as toluene and a xylene, are desirable and otherwise use together alcohols solvents, such as ketones, such as ester solvents, such as ethyl acetate and butyl acetate, a methyl ethyl ketone, and methyl isobutyl ketone,

ethanol, isopropanol, and n-butanol, an aliphatic series system solvent, an annular aliphatic series system solvent, etc. The radical generating agent described above as a polymerization initiator can use it as it is.

[0025] As for the weight ratio of the monomer which has an ethylene nature unsaturated bond and a hydroxyl group in the monomer which has an ethylene nature unsaturated bond in the carboxyl group content chlorinated polyolefins of this invention, and 1 molecule, and 1 molecule, carboxyl group content chlorinated polyolefins / [1 Monomer which contains ethylene nature unsaturated bond in molecule] + [monomer which contains ethylene nature unsaturated bond and hydroxyl group in 1 molecule] = 90 / 10 - 10/90 are desirable. If there are too many carboxyl group content chlorinated polyolefins, weatherability will worsen, and if too few, the adhesion over polyolefine system resin will worsen.

[0026] Although it may coat as it is and you may use, a pigment, a solvent, other additives, for example, an ultraviolet ray absorbent, an antioxidant, and a pigment sedimentation inhibitor are added, and the binder resin constituent of this invention can be dispersedly kneading and used as a coating or printing ink. Furthermore, it can be used also as the adhesives of various plastics including a polypropylene resin, or a primer for paint. Although the loadings of a binder resin constituent can be adjusted to arbitration according to the purpose, its 10 % of the weight or more is desirable from the point of the adhesion over various plastics, and the cohesive force of a constituent.

[0027] Moreover, although the paint film physical properties which maintained balance only by it are shown, if this binder resin constituent is required, even if it adds further and it uses an alkyd resin, acrylic resin, the poly acrylic polyol, polyester resin, polyester polyol, polyether resin, polyether polyol, polyurethane resin, chlorinated polyolefins, etc., it will not interfere.

[0028]

[Function] The place by which it is characterized [of this invention] has adhesion in obtaining the binder resin constituent in which good adhesion is shown also to the difficult polyolefine conventionally while improving the reactivity of the chlorinated polyolefins in which are carrying out the graft copolymerization of the monomer containing a hydroxyl group to an ethylene nature unsaturated bond, and reactivity is essentially inferior in the monomer which contains an ethylene nature unsaturated bond in carboxyl group content chlorinated polyolefins and 1 molecule, and 1 molecule, and this monomer and obtaining uniform and transparent reaction mixture.

[0029] Here, the polymerization object of the monomer which contains an ethylene nature unsaturated bond in 1 molecule is a component indispensable in order to form the frame of binder resin. Moreover, although carboxyl group content chlorinated polyolefins also accomplish the frame of binder resin, it is a component for mainly giving the adhesion over polyolefine.

[0030] The dimethyl trimethylene carbonate denaturation (meta) acrylic ester which is the monomer which contains an ethylene nature unsaturated bond and a hydroxyl group in 1 molecule is an important component for obtaining uniform and transparent reaction mixture. That is, since the hydroxyl group in this monomer and the carboxyl group in carboxyl group content chlorinated polyolefins carry out an esterification reaction, this is made into a reacting point and graft copolymerization advances, it is thought that uniform and transparent reaction mixture is obtained.

[0031] When a graft copolymerization reaction is performed on the other hand using hydroxyl-group content monomers other than this monomer, for example, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 2-hydroxy butyl (meta) acrylate, etc., From reaction mixture carrying out two-layer separation, or becoming cloudy, although the clear reason is unknown When the reaction of the carboxyl group content chlorinated polyolefins used for this invention and dimethyl trimethylene carbonate denaturation (meta) acrylic ester and a reaction with other monomers advance with sufficient balance It is thought that the graft copolymer which maintained the uniform and transparent balance which otherwise does not look at an example was able to be obtained.

[0032]

[Example] Next, an example explains this invention to a detail further.

[0033] (Example -1 of manufacture) The melt viscosity in 180 degrees C is 2500 mPa-s. It put in into

the 3 TSU openings flask furnished with a cooling pipe for an ethylene content to flow back an agitator and a monomer in 6kg of six-mol ethylene [which is %]-propylene copolymerization objects, and dissolved completely in the oil bath kept constant at 180 degrees C. After performing the nitrogen purge in a flask for about 10 minutes, it supplied having poured [240g] it for 5 minutes performing churning, and then G tert-*****-***** 24g was dissolved in the 50ml heptane, and with the metering pump, it applied for about 30 minutes and added. After keeping the inside of a system at 180 degrees C at this time and continuing a reaction further for about 1 hour, decompressing the inside of a flask with an aspirator, it applied for about 30 minutes and the unreacted maleic anhydride was removed. Next, this product is supplied to the reaction vessel by which glass lining was carried out, 100l. chloroform is added, and it is 2.5kg/cm². Irradiating ultraviolet rays, after dissolving completely at 110 degrees C in the bottom of a pressure, chlorine gas was blown and the chlorination reaction was performed. The chloroform of a solvent was distilled off by the evaporator after reaction termination, the toluene permutation was carried out, in order to press down a demineralization acid, the sec-buthylphenyl glycidyl ether which is a mono-epoxy compound was added 4% of the weight to solid content as a stabilizer for suppressing the rise of the solution viscosity by bridge formation during preservation, and solid content obtained the toluene solution of 20% of the weight of a carboxyl group content chlorination ethylene-propylene copolymerization object. The rate of a maleic-anhydride graft of the chlorine content at this time was 2.5 % of the weight (opposite solid content) at 21.2 % of the weight (opposite solid content).

[0034] (Example -2 of manufacture) Except that number average molecular weight used about 15000 isotactic polypropylene 6kg, 420g [of maleic anhydrides], and G tert-butyl peroxide 42g, the same melting reaction as the example 1 of manufacture was performed, and, subsequently the chlorination reaction was performed similarly. After carrying out vacuum concentration of the chloroform of a solvent by the evaporator and adding sec-buthylphenyl glycidyl ether 4% of the weight to solid content, the solid of the carboxyl group content chlorination polypropylene which removed chloroform completely with the extruder with a vent equipped with the vent-port for carrying out reduced pressure distilling off of the reaction solvent, extruded in the shape of a strand, cooled with water, and was pelletized by the water cooling type pelletizer (model made from limited-company *****: KM-150) was obtained. The rate of a maleic-anhydride graft of the chlorine content at this time was 4.3 % of the weight (opposite solid content) at 24.3 % of the weight (opposite solid content).

[0035] (Example -3 of manufacture) After the melt index's having supplied isotactic polypropylene 6kg of 14 g/min (it measured according to ASTM D1238-62T) to the reaction vessel by which glass lining was carried out, adding the 100l. carbon tetrachloride and fully dissolving under 2kg/cm² conditions of - 110 degree C, irradiating ultraviolet rays, chlorine gas was blown from the reaction vessel pars basilaris ossis occipitalis, and the reaction mixture whose chlorine content is 30 % of the weight was obtained. Next, it is tert as a stabilizer after condensing by the evaporator. - Buthylphenyl glycidyl ether was added 4% of the weight to solid content, the carbon tetrachloride which is a reaction solvent was permuted by toluene, and the toluene solution of the chlorination polypropylene whose solid content concentration is 30 % of the weight was obtained. Next, having put into the three necked flask furnished with the cooling pipe for flowing back an agitator, a dropping funnel, and a monomer in 1000g of this chlorination polypropylene solution, and nitrogen having permuted the inside of a flask, and agitating at 90 degrees C, 3g of benzoyl peroxide was added and it was agitated for about 30 minutes. Next, it supplied from the dropping funnel, having covered [15g] it for about 30 minutes, after reacting for further 3 hours, concentration adjustment was performed, and solid content obtained the toluene solution of 20% of the weight of carboxyl group content chlorination polypropylene. The rate of a methacrylic-acid graft of the chlorine content at this time was 4.7 % of the weight (opposite solid content) at 27.6 % of the weight (opposite solid content).

[0036] The carboxyl group content chlorinated polyolefins obtained in the examples 1-3 of manufacture were packed into Table 1.

[0037]

[Table 1]

表1 製造例1～3のカルボキシル基含有塩素化ポリオレフィンの内容

	製造例-1	製造例-2	製造例-3
原料モノマー (固形分)	エチレン・ブチレン共重合体 2.0重量%	ポリブチレン・ブチレン (ペレット) 2.4.3重量%	ポリブチレン・ブチレン 2.0重量%
塩素含有率 (対固形分)	2.1.2重量%	2.4.3重量%	2.7.6重量%
カルボキシル基 グラフト率 (対固形分)	2.5重量% (無水マレイン酸グラフト率)	4.3重量% (無水マレイン酸グラフト率)	4.7重量% (マレイン酸グラフト率)

[0038] (Example -1) In the flask furnished with the cooling pipe for flowing back an agitator, a thermometer, and a monomer, 500g of carboxyl group content chlorinated polyolefins and toluene 250g obtained in the example -1 of manufacture were supplied, and it warmed at 85 degrees C. Next, methyl methacrylate 245g, cyclohexyl methacrylate 100g, 10g of methacrylic acids, and dimethyl trimethylene carbonate (1 ****) after adding benzoyl peroxide 5g and agitating for 30 minutes 40g (Following HEAC is called) of denaturation ethyl acrylates was added over about 3 hours, the graft copolymerization reaction was performed further for about 7 hours, solid content concentration was adjusted to the toluene solution 40% of the weight, and the uniform and transparent binder resin solution was obtained. Next, by the approach shown below, the primer trial, the coating trial, and the ink test were performed. The result was shown in Tables 2, 3, and 4.

[0039] (Example -2) 150g (pellet) of carboxyl group content chlorinated-polyolefins solids obtained in the example -2 of manufacture is dissolved in toluene 660g. Benzoyl peroxide 5g, methyl methacrylate 200g, 70g of n-butyl methacrylates, Except extracting styrene 30g, 10g of acrylic acids, and 35g (Following HEMAC being called) of dimethyl trimethylene carbonate (1 ****) denaturation ethyl methacrylates The graft copolymerization reaction was performed by the same approach as an example 1, solid content concentration was adjusted to the toluene solution 40% of the weight, and the uniform and transparent binder resin solution was obtained. Next, by the approach shown below, the primer trial, the coating trial, and the ink test were performed. The result was shown in Tables 2, 3, and 4.

[0040] (Example -3) Except extracting 875g [of carboxyl group content chlorinated polyolefins obtained in the example 3 of manufacture], and benzoyl peroxide 5g, methyl methacrylate 155g, 125g of n-butyl methacrylates, 5g of methacrylic acids, and HEAC35g, the graft copolymerization reaction was performed by the same approach as an example 1, solid content concentration was adjusted to the toluene solution 40% of the weight, and the uniform and transparent binder resin solution was obtained. Next, by the approach shown below, the primer trial, the coating trial, and the ink test were performed. The result was shown in Tables 2, 3, and 4.

[0041] (Example -1 of a comparison) It chlorinated by blowing chlorine gas, number average molecular weight having dissolved isotactic polypropylene 5kg of 5000 in 80l. of carbon tetrachlorides under pressurization (2kg/cm²) at homogeneity, and irradiating ultraviolet rays at the temperature of 100-110 degrees C. When chlorine content reached to about 20% of the weight, chlorine gas was changed to the mixed gas from which about 10/100 of volume ratios of chlorine/air is set to 90, and it chlorinated gently, performing oxidation treatment. Carrying out trace measurement of the functional-group characteristic shown below with an infrared spectrophotometer, the functional-group characteristic sampled the sample whose chlorine content is 30.2 % of the weight by 15.5, and distilled off the carbon tetrachloride, the toluene permutation was carried out and extent of oxidation treatment obtained the oxidized chlorination polypropylene whose solid content concentration is 50 % of the weight.

Functional-group characteristic =(absorbance of absorbance / 2970cm⁻¹ of 1730cm⁻¹) x100[0042] Next, chlorination polypropylene 375g obtained in the example 1 of manufacture, oxidized chlorination polypropylene 50g, toluene 325g, benzoyl peroxide 5g, methyl methacrylate 255g, 10g of methacrylic acids, cyclohexyl methacrylate 110g and 2 - Except extracting hydroxyethyl acrylate (2HEA being

called below) 20g, the graft copolymerization reaction was performed by the same approach as an example 1, solid content concentration was adjusted to the toluene solution 40% of the weight, and the uniform and transparent binder resin solution was obtained. Next, by the approach shown below, the primer trial, the coating trial, and the ink test were performed. The result was shown in Tables 2, 3, and 4.

[0043] (Example -2 of a comparison) Except extracting chlorination polypropylene 500g [which was obtained in the example 1 of manufacture], toluene 250g, benzoyl peroxide 5g, methyl methacrylate 255g, 10g [of methacrylic acids], and cyclohexyl methacrylate 110g, and 2HIEA20g, the graft copolymerization reaction was performed by the same approach as an example 1, and solid content concentration was adjusted to the toluene solution 40% of the weight. The binder resin solution became cloudy, and when put, it carried out bilayer separation. Next, by the approach shown below, the primer trial, the coating trial, and the ink test were performed. The result was shown in Tables 2, 3, and 4.

[0044]

[Primer test method]

1) Combination presentation of a primer Binder resin solution constituent (40% toluene solution) -- The 100 weight sections Titanium dioxide -- 20 ** carbon black -- After kneading the adjustment above-mentioned presentation of 4**0.2 primer by the sand mill for about 1 hour, it diluted with the xylene and adjusted so that it might become 12 - 13 seconds / 20 degrees C by Ford cup #4.

3) A washing ** primer can be burned with an air spray at a paint (10-15 micrometers of thickness) ** room temperature, desiccation ** KURIYA can be desiccation ** Burned for 20 - 30 minutes for 15 - 20 minutes at a spray painting (2 liquid hardening mold urethane coating, 30 micrometers of thickness) ** room temperature with method-of-application polypropylene plate (TX-933A, Mitsubishi Chemical (stock) make) ** neutral detergent (for [80-degree-C] -30 minutes), and it is operation [0045] about the trial of an after [standing] paint film at ** 24-hour room temperature. (The evaluation approach)

- The grid of 100 pieces which reaches at intervals of 1mm on the adhesive painted surface at a base was made, cellophane adhesive tape was stuck on it and the number of the grids which lengthen, remove and remain in the direction of 180 degree was investigated.

- The damp-proof paint plate was left for 240 hours in 50 degrees C and the ambient atmosphere of 98% of relative humidity, and the condition of a paint film and adhesion were investigated.

- It is a warm water-proof nature paint plate to 40-degree C warm water 240 Time amount immersion was carried out and the condition of a paint film and adhesion were investigated.

- The scratch (x mark) which reaches a base was put in on the gasoline-proof nature painted surface, it was immersed in a gasoline / ethanol =9 / 1 (volume ratio), and the condition of a paint film was investigated.

- Ultraviolet resistance was examined for the ultraviolet resistance paint plate with the QUV weather meter (Q-PANEL COMPANY make). The judgment of a result judged degradation of a paint film by the adhesion for every QUV exposure time.

[0046]

[Coating test method]

1) Combination presentation of a coating Binder resin solution constituent (40% toluene solution) -- The 100 weight sections Titanium dioxide -- 4.5 ** carbon black -- 0.5 ** rouge -- 2 ** talc -- 15 ** silica flattening agent -- After kneading the adjustment above-mentioned presentation of 3 **2 coating by the sand mill for about 1 hour, it diluted with the xylene and adjusted so that it might become the viscosity of 12 - 13 seconds / 20 degrees C by Ford cup #4.

3) A washing ** coating can be desiccation ** Burned for 20 - 30 minutes at a paint (30 micrometers of thickness) ** room temperature at an air spray with method-of-application polypropylene plate (TX-933A, Mitsubishi Chemical (stock) make) ** neutral detergent (for [60-degree-C] -30 minutes), and it is operation [0047] about the trial of an after [standing] paint film at ** 48-hour room temperature. (The evaluation approach)

- About adhesion, moisture resistance, and warm water-proof nature, it is the same as the above.

- The cloth which infiltrated butter on the butyrateous-proof painted surface was stuck, and after

washing out completely the butter which remains on the painted surface after standing for seven days at 70 degrees C, the adhesion of a paint film was investigated.

- The paint plate was immersed in the alkali water solution of alkali-proof 0.1 convention for 120 hours, and the condition of a paint film was investigated.

[0048]

[The ink test approach]

1) Combination presentation of ink [White ink]

Binder resin solution constituent (40% toluene solution) -- The 100 weight sections Titanium dioxide -- 30 ** [red ink]

Binder resin solution constituent (40% toluene solution) -- The 100 weight sections Carmine 6BN -- 14 ** * carmine 6BN: Azo system organic pigment (TOYO INK MFG. (stock) make)

2) After milling the adjustment above-mentioned presentation of ink by the sand mill for 3 hours, it diluted with toluene and adjusted so that it might become the viscosity of 25 - 30 seconds / 20 degrees C from #3 ZAN cup.

[0049] (The evaluation approach)

- after carrying out coating of the ink adjusted by the approach of the Scotch tape friction test above to the unsettled polypropylene film (below unsettled -- PP is called) and the corona-discharge-treatment polypropylene film (Processing PP is called below) by coating rod #14, respectively and drying at a room temperature for 24 hours, cellophane adhesive tape was stuck on the ink coating side, and the desquamative state of the coating side when removing at a stretch was investigated.

- unsettled by the same approach as a heat-sealing strength test Scotch tape friction test -- the ink coating side after carrying out coating of the ink to Processing PP with PP and drying at a room temperature for 24 hours -- superposition and 120 degree-C-1 kg/cm² It heat sealed on the sticking-by-pressure conditions for 2 seconds, and 180-degree peel strength was measured in 24 hours after tensilon (hauling rate: 50 mm/min).

[0050]

[Table 2]

表2 バインダー樹脂溶液の状態及びプライマー試験結果

	実施例-1	実施例-2	実施例-3	比較例-1	比較例-2
バインダー樹脂溶液の状態	均一透明	均一透明	均一透明	均一透明	白濁二層分離
付着性	100/100	100/100	100/100	100/100	100/100
耐油性	異常なし 100/100	異常なし 100/100	異常なし 100/100	異常なし 100/100	アリスター発生 90/100
耐水性	異常なし 100/100	異常なし 100/100	異常なし 100/100	異常なし 100/100	アリスター発生 85/100
耐ガンリン性	2時間浸漬後 異常なし	2時間浸漬後 異常なし	2時間浸漬後 異常なし	1時間浸漬後 塗膜剥離	1時間浸漬後 塗膜剥離
耐紫外線性 (QUV暴露時間)					
0	100/100	100/100	100/100	100/100	100/100
200	100/100	100/100	100/100	100/100	95/100
500	100/100	100/100	100/100	85/100	85/100
1000	100/100	100/100	100/100	35/100	20/100

[0051]

[Table 3]

表3 塗料試験結果

	実施例-1	実施例-2	実施例-3	比較例-1	比較例-2
付着性	100/100	100/100	100/100	100/100	100/100
耐油性	異常なし	異常なし	異常なし	異常なし	ブリスト-発生
	100/100	100/100	100/100	100/100	90/100
耐水性	異常なし	異常なし	異常なし	異常なし	ブリスト-発生
	100/100	100/100	100/100	100/100	85/100
耐バタ-性	100/100	100/100	100/100	70/100	65/100
耐アルカリ性	異常なし	異常なし	異常なし	ブリスト-発生	ブリスト-発生

[0052]

[Table 4]

表4 インキ試験結果

試験	インキ色	実施例-1		実施例-2		実施例-3		比較例-1		比較例-2	
		白	赤	白	赤	白	赤	白	赤	白	赤
付着性	未処理PP	良好	良好	良好	良好	良好	良好	不良	不良	不良	不良
剝離	処理PP	良好	良好	良好	良好	良好	良好	良好	良好	不良	不良
ヒートショック	未処理PP	180	150	173	158	150	143	100	95	95	80
度 (g/cm)	処理PP	315	248	315	285	300	225	190	150	150	110

[0053]

[Effect of the Invention] The example 1 of a comparison is the binder resin constituent which this invention person etc. already proposed by Japanese Patent Application No. 506386 [eight to]. The example 2 of a comparison is the binder resin constituent compounded using HEAC used by the invention in this application, and the monomer which has the partial saturation radicals and hydroxyl groups other than HEMAC. Although the shape of transparent liquid with uniform example and example 1 of a comparison is shown [in / for these / the condition of a binder resin solution] as compared with the binder resin of an example, it turns out that the example 2 of a comparison serves as nebula bilayer separation, and the reactivity of graft copolymerization is inferior (Table 2).

[0054] Compared with an example, the example 1 of a comparison has gasoline-proof nature and ultraviolet resistance inferior in the primer engine performance, and the example 2 of a comparison is inferior in moisture resistance, warm water-proof nature, gasoline-proof nature, and ultraviolet resistance (Table 2). Although the same inclination is shown also in coating physical properties, in the example of a comparison, butyraceous one-proof and alkali resistance are inferior to the example (Table 3). An example cannot necessarily say that it is enough in the example of a comparison to good adhesion being shown to PP film about ink physical properties (Table 4). It turns out that the binder resin constituent of the invention in this application is more useful than the above result.

[Translation done.]